THE STRUCTURE OF THE $Mo_6Cl_{14}^{--}$ COMPLEX IN THE CRYSTAL $(NH_4)_2(Mo_6Cl_8)Cl_6 \cdot H_2O$

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Cyrill Brosset has determined the crystal structures of the bipositive molybdenum compounds $(Mo_6Cl_8)(OH)_4 \cdot 14H_2O$[1] and $(Mo_6Cl_8)(Cl_4 \cdot 2H_2O) \cdot 6H_2O$[2] and has found that the basic structural unit for these compounds is a $(Mo_6Cl_8)X_6$ group in which X is oxygen or chlorine. The structure of this group can be visualized as follows (Fig. 1). The molybdenum atoms are at the corners of a nearly regular octahedron of edge 2.63 Å, eight chlorine atoms are at the corners of a symmetrically circumscribed cube such that the shortest Mo–Cl distance is 2.56 Å, and the six X atoms are at the corners of a larger octahedron, one X being bonded to each molybdenum atom.

Some years ago, at the suggestion of Professor Linus Pauling, I began an x-ray study of the compound $(NH_4)_2(Mo_6Cl_8)Cl_6 \cdot H_2O$. It forms crystals with space group C_s^4-Cc and unit cell parameters $a_1 = 19.33$ Å, $a_2 = 14.93$ Å, $a_3 = 9.16$ Å, and $\beta = 115.2°$. The volume of the unit cell is 2390 Å,[3] which, for four formulae per cell, leads to calculated density 3.12 g. cm.$^{-3}$, in good agreement with the observed density 3.09 g. cm.$^{-3}$, determined by flotation.

By applying the radial distribution method to a powder photograph of this compound, I have found that it contains the group $(Mo_6Cl_8)Cl_6^{--}$ with the structure described above. The intensity function used was

$$I'(s) = \sum_i I_i e^{-C(s-s_i)^2}, \tag{1}$$

where I_i is visually estimated intensity of the ith powder line and $s = \frac{4\pi \sin\theta}{\lambda}$, θ being the Bragg angle. It is readily shown that, to a good approximation, $I'(s)$ is given by

$$I'(s) = K \sum_{i,j} A_{ij} \sin s r_{ij}, \tag{2}$$

where

$$A_{ij} = \frac{\overline{f_i f_j}}{r_{ij}} e^{-(r_{ij}^2/4C)}.$$

The radial distribution integral was then calculated from the equation

$$rD(r) = \int_0^{s_{max.}} e^{-as^2} I'(s) \sin sr \, ds \tag{3}$$

by means of the punched card technique developed in these Laboratories for electron diffraction investigations.[3] The radial distribution function is then interpreted in terms of the structure by the relationship

$$rD(r) = \sum_{i,j} \frac{A_{ij}}{4} \sqrt{\frac{\pi}{a}} e^{-[(r-r_{ij})^2/4a]}, \qquad (4)$$

the sum being over all of the non-zero distances in the proposed structure and A_{ij} being defined above. The function $I'(s)$ has the advantage that it is a smooth function of s and can therefore be treated in much the same

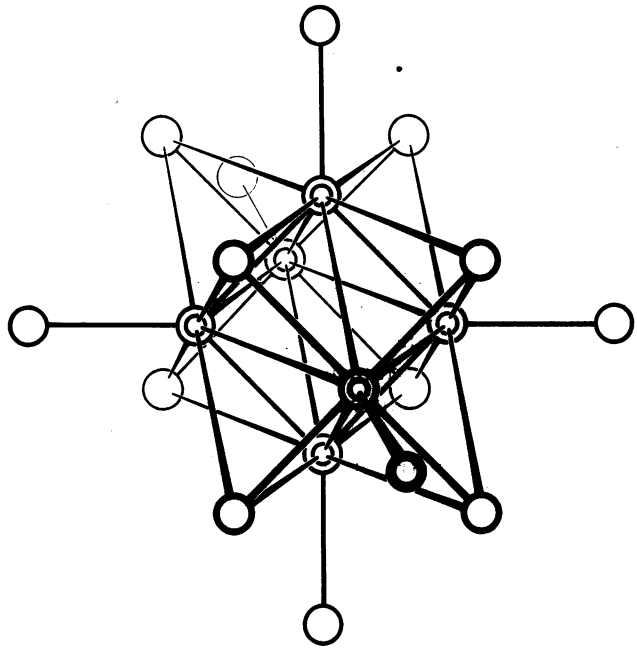

FIGURE 1

The $(Mo_6Cl_8)Cl_6^{--}$ ion, double circles are Mo atoms; single circles are chlorine atoms.

way as an electron diffraction scattering curve; for instance, theoretical $I'(s)$ curves can readily be calculated for any proposed structure by means of equation (2). The function $I'(s)$ and the radial distribution function obtained therefrom are shown in figure 2. The $(Mo_6Cl_8)Cl_6^{--}$ group would probably have, following the work of Brosset, the following parameters:

Shortest Mo–Mo	= 2.63 Å (average)
Mo–Cl (cubic Cl)	= 2.56 Å (average)
Mo–Cl (octahedral Cl)	= 2.43 Å

A radial distribution function corresponding to this model calculated from equation (4) is shown in figure 2. The agreement with the experimental radial distribution function is good, the only serious discrepancy out to about 5 Å being the greater height of the peak near 3.6 Å in the experimental curve. This is explained by the fact that there are additional

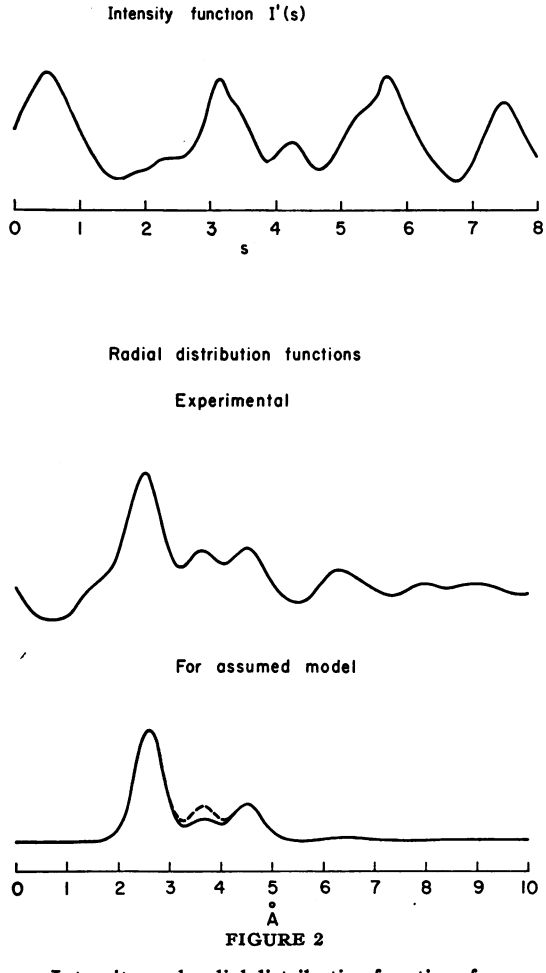

FIGURE 2

Intensity and radial distribution functions for $(NH_4)_2(Mo_6Cl_8)Cl_6 \cdot H_2O$.

Cl...Cl distances of about 3.60 Å in the crystal due to intermolecular contacts. If the reasonable assumption is made that each octahedral chlorine atom makes van der Waals' contact with six chlorines in different molecules and that each cubic chlorine atom makes contact with three,

the theoretical radial distribution function becomes as indicated by the dotted line in figure 2; the heights are now in excellent agreement. The positions and relative heights of the maxima less than 5 Å in the two radial distribution functions are

EXPERIMENTAL		THEORETICAL	
HEIGHT	POSITION	HEIGHT	POSITION
100	2.53 Å	100	2.59 Å
31.8	3.63 Å	32.0	3.65 Å
33.6	4.50 Å	34.4	4.50 Å

The agreement provides very strong evidence that the $(Mo_6Cl_8)X_6$ group found by Brosset is present in $(NH_4)_2(Mo_6Cl_8)Cl_6 \cdot H_2O$.

Space group and packing considerations lead to the conclusion that the $(Mo_6Cl_8)Cl_6^{--}$ groups are arranged in nearly directly superposed hexagonal layers parallel to (001). Each group has four neighboring groups at about 8.75 Å and two at 9.16 Å in the same layer; the interlayer spacing is 8.76 Å.

* Contribution No. 1432.

[1] Brosset, Cyrill, *Arkiv. Kemi, Mineral. Geol.*, **A20** (1945).

[2] Brosset, Cyrill, *Ibid.*, **A22** (1946).

[3] Shaffer, P. A., Schomaker, V., and Pauling, L., *J. Chem. Phys.*, **14**, 659–64 (1946).

FACTORS GOVERNING SEXUAL SELECTION AS AN ISOLATING MECHANISM IN THE POECILIID FISH LEBISTES RETICULATUS

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In a previous paper[1] it was pointed out that three species of small viviparous Poeciliid fishes, *Poecilia vivipara*, *Micropoecilia parae*, and *Lebistes reticulatus*, form an unusually intimate sympatric association in certain brackish coastal waters of the island of Trinidad. The geographic range of all three species is similar, *P. vivipara* and *L. reticulatus* being characteristic inhabitants of the coastal streams and lagoons of northeastern South America and the immediately adjacent islands, while *M. parae* is represented in the same mainland areas either by the typical species or by morphologically distinguishable but closely related forms. The ecological preferences of the three species are closely similar. All are primarily surface feeders in warm shallow waters. In Trinidad, *P. vivipara* and *M. parae* are confined to brackish coastal waters, while *L. reticulatus* is a common inhabitant of all bodies of water of any size, ranging from mountain streams